INHIBITING DEPOSIT FORMATION BY BACTERIA ON SURFACES OF PAPER AND BOARD MACHINES

PCT/FI2003/000833

Patenttinumero: WO2004040982
Julkaisupäivä: 2004-05-21
Keksijä: VAEAETAENEN PENTTI (FI); SALKINOJA-SALONEN MIRJA (FI)
Hakija: KEMIRA OYJ (FI); VAEAETAENEN PENTTI (FI); SALKINOJA-SALONEN MIRJA (FI)
Patenttiluokitus
- kansainvälinen ***A01N43/16; A01N65/00; A61L2/18; C02F1/50; D21H21/04;*** **A01N43/02; A01N65/00; A61L2/18; C02F1/50; D21H21/00;** (IPC1-7): A01N65/00; C02F1/50; D21H21/02
- eurooppalainen A01N43/16; A01N65/00; A61L2/18; C02F1/50; D21H21/04
Hakemusnumero: WO2003FI00833 20031106
Etuoikeusnumero(t): FI20020001987 20021106

Julkaisuja muista maista

AU2003276301 (A
FI115502B (B)

Viitejulkaisut:

US2002051819
WO02078450
US6267897
WO0059834
WO0026466
Lue lisää >>

Report a data error he

Tiivistelmä **WO2004040982**

The invention relates to a method of inhibiting the deposit formation caused by thermophilic adhering bacteria, Deinococcus geothermalic in particular, on surfaces of paper or board machines, or removing such deposits from the said surafces so that a concentration of at least one plant extract prepared from wood, bushes or woody, shrubby plants, or at least one plant-based substance, such as betulin or a flavonol or a mixture thereof, is added to the circulation waters of paper or board machines, the concentration being effective against thermophilic adhering bacteria.

(12) **PATENTTIJULKAISU**
PATENTSKRIFT

FI0000115502B

(10) **FI 115502 B**

(45) Patentti myönnetty - Patent beviljats **31.05.2005**

(51) Kv.lk.7 - Int.kl.7

A01N 65/00, 43/16, 45/00, C02F 1/50
// D21H 21/04, C02F 103:28

(21) Patenttihakemus - Patentansökning **20021987**

(22) Hakemispäivä - Ansökningsdag **06.11.2002**

(24) Alkupäivä - Löpdag **06.11.2002**

(41) Tullut julkiseksi - Blivit offentlig **07.05.2004**

SUOMI – FINLAND
(FI)

PATENTTI- JA REKISTERIHALLITUS
PATENT- OCH REGISTERSTYRELSEN

(73) Haltija - Innehavare

1 •Kemira Oyj, Porkkalankatu 3, 00180 Helsinki, SUOMI - FINLAND, (FI)

(72) Keksijä - Uppfinnare

1 •Väätänen, Pentti, Erämiehenkatu 41 C, 65370 Vaasa, SUOMI - FINLAND, (FI)
2 •Salkinoja-Salonen, Mirja, Nastolantie 26, 00600 Helsinki, SUOMI - FINLAND, (FI)

(74) Asiamies - Ombud: Berggren Oy Ab
Jaakonkatu 3 A, 00100 Helsinki

(54) Keksinnön nimitys - Uppfinningens benämning

Bakteerien aiheuttaman kertymänmuodostuksen estäminen paperi- ja kartonkikoneiden pinnoille
Förhindrande av avlagringsbildning förorsakad av bakterier på ytor av pappers- och kartongmaskiner

(56) Viitejulkaisut - Anförda publikationer

EP 778244 A1, WO 00/26466 A1, WO 00/59834 A1, WO 01/68530 A2, WO 02/078450 A1

(57) Tiivistelmä - Sammandrag

Keksintö koskee menetelmää termofiilisten tarttujabakteerien, erityisesti Deinococcus geothermalis, aiheuttaman kertymänmuodostuksen estämiseksi paperi- tai kartonkikoneiden pinnoille tai tällaisten kertymien poistamiseksi mainituilta pinnoilta siten, että paperi- tai kartonkikoneiden kiertovesiin lisätään termofiilisiin tarttujabakteereihin tehoava pitoisuus ainakin yhtä puusta, pensaasta tai varpukasvista valmistettua kasviuutetta tai ainakin yhtä kasviperäistä ainetta, kuten betuliinia tai flavonolia, tai niiden seosta.

Uppfinningen avser ett förfarande för förhindrande av avlagringsbildning förorsakad av termofila vidhäftningsbakterier, speciellt Deinococcus geothermalis, på ytor av pappers- eller kartongmaskiner eller för avlägsnande av dylika avlagringar från nämnda ytor genom att i pappers- eller kartongmaskiners cirkulationsvatten tillsätta en på termofila vidhäftningsbakterier verkande effektiv halt av åtminstone ett växtextrakt framställt från trä, en buske eller en risväxt eller åtminstone en substans av vegetabiliskt ursprung, såsom betulin eller flavonol, eller en blandning därav.

Inhibiting deposit formation by bacteria on surfaces of paper and board machines

The invention relates to a method of inhibiting the deposit formation by thermophilic bacteria on surfaces of paper or board machines or removing such deposits from the said surfaces.

Field of the invention and prior art

To ensure a smooth production of paper and board machines, special chemicals, anti-microbial agents, are used to inhibit the growth of detrimental microbes in the process waters and on the surfaces thereof. These should be approved in advance. The deposits, which detach from the surfaces and cause breaks and idle time, contain detrimental bacteria as well as other bacteria, fibres, fibrils, pitch, pigments and other raw materials of papermaking. Such deposits formed by bacteria are also called biofilms. According to the newest studies (M. Kolari, J. Nuutinen and M.S. Salkinoja-Salonen, Mechanism of biofilm formation in paper machine by *Bacillus* species: the role of *Deinococcus geothermalis*, Journal of Industrial Microbiology & Biotechnology (2001) 27, pp. 343-351), one vital factor in the deposit formation is a so-called primary adhering bacterium (*Deinococcus geothermalis*), which can start the deposit formation. This bacterium is fairly common in paper machines. The purpose of preventing this bacterium from adhering to steel surfaces is thus to decrease the deposit formation that is harmful to the runnability of paper machines.

The patent publication US 6 267 897 B discloses a method of preventing biofilm formation in commercial and industrial water systems by adding an essential oil into the system. As examples of water systems, the publication cites, among others, cooling water, water in the food industry, systems of pulp and paper mills, pasteurizing apparatuses of breweries, fresh-water systems, etc. This patent publication describes a test, which studies the biofilm formation of *Sphaerotilus natans*, a slime-forming microorganism, which commonly occurs in paper mills, on glass surfaces. The results indicate that eucalyptus oil, cinnamon oil, and tea tree oil prevent the attachment of the studied bacterium on glass surfaces more effectively than the copolymer of ethylene oxide and propylene oxide that was used as a reference compound. According to this patent publication, eucalyptus oil and cinnamon oil, which are commercial drug preparations, are particularly advantageous essential oils and prepared by distillation in steam, as is well known. The other essential oils specified in this patent publication are made by distillation in steam or by compression.

The S. *natans* bacterium is not found in modern hot paper machines, because it cannot grow at temperatures of 50 to 60°C. Instead, a truly problematic bacterium in the paper machines of today is the *Deinococcus geothermalis*, which grows at high temperatures (56 to 57°C at a maximum). On the basis of the studies conducted, it can be established that the essential oils were actually not at all capable of preventing the deposit formation by the problematic bacterium *Deinococcus geothermalis*, (see the Reference Example 2 presented hereinafter).

The present invention is particularly intended to preventing such deposit formation, wherein an essential part comprises the really problematic bacterium *D. geothermalis* that grows at the high temperatures (about 50 to 60°C) of today's paper machines.

Accordingly, the purpose of the invention is to provide a method and an agent used therein, which can be used to effectively prevent the deposit formation caused by thermophilic bacteria, the *Deinococcus geothermalis* bacterium in particular, on surfaces of paper or board machines.

Description of the invention

It has now been discovered that by using natural plant extracts and certain plant-based substances (betulin and flavonols in particular), the formation of detrimental deposits in paper and board machines can be prevented by interfering with the adhesion of the actual problematic bacteria on the surfaces of the tube systems and the wet end. By using these substances, breaks and idle time can be reduced, which are caused by deposits that form on the surfaces of paper and board machines and detach from them, if the formation thereof is not inhibited. According to the laboratory research conducted, the plant extracts effectively (91 to 99.7%) prevented the adhesion of a significant factor of the deposits, namely the *Deinococcus geothermalis* bacterium, on the paper machine steal surfaces (AISI 316). The plant-based substances studied (betulin and flavonols) variably prevented (84 to 99.95%) the adhesion of the said deinococcus to the steal, depending on the substance.

Thus, the invention, provides a method of inhibiting the deposit formation caused by thermophilic adhering bacteria on surfaces of paper or board machines, or removing such deposits from the said surfaces, which method is characterized in that a concentration of at least one plant extract or at least one plant-based substance or a mixture thereof is added to the circulation waters of paper or board machines, the concentration being effective against thermophilic adhering bacteria.

The said plant extract may originate from trees, bushes or woody, shrubby plants, particularly from one of the following plants of parts of plants: deciduous tree, bark of a conifer, decayed conifer or a woody, shrubby plant.

Examples of suitable deciduous trees include rowan tree, birch, maple and willow. Examples of suitable woody, shrubby plants include lingonberry and blueberry. The said bark of a conifer is preferably pine bark and the said decayed conifer is preferably decayed spruce branches.

The said plant extract can be obtained by extracting the plant or part of it with a suitable solvent or a mixture of solvents. One preferable solvent is ethanol or acetone or a mixture thereof. When using the mixture of ethanol and acetone, the volumetric ratio of ethanol to acetone may be in a range of 99:1 – 1:99, preferably within 95:5 – 5:95. Other solvents suitable for the extraction include methanol, hexane and chloroform. The mixtures of the solvents presented herein can also be used.

In this connection, the plant-based substance refers to a natural substance isolated from a plant, or a synthetic equivalent or derivative thereof. This substance as well as the said plant extract should have the ability to prevent the deposit-formation by thermophilic bacteria on surfaces and/or the ability to remove such deposits from the surfaces.

The said plant-based substance is preferably betulin or a flavonol, such as pentahydroxy flavone or trihydroxy flavone or a mixture thereof. Betulin is found in birch bark and flavonols can be obtained from the blossoms of the plants. These substances can also be prepared synthetically.

The plant extract or the plant-based substance or a mixture thereof is added to the circulation water of paper or board machines so as to obtain a product concentration, which may be 1 to 1000 ppm, preferably 10 to 500 ppm, and especially preferably 20 to 250 ppm as calculated from the dry weight of the plant extract or the plant-based substance.

The plant extract or the plant-based substance or the mixture thereof can be dosed into the circulation water of the paper or board machines either 2 to 8 times a day in cycles, or as one single dose per day.

The plant extract of the plant-based substance or a mixture thereof can also be dosed into a container in large doses of 500 to 5000 ppm as calculated from the dry weight of the plant extract or the plant-based substance, so as to detach the adhering bacteria from the container surfaces by means of so-called shock dosing.

According to the invention, the raw extracts obtained from the said plants, or more effective components isolated from these raw extracts can be used.

The invention also relates to the use of the said plant extract or the plant-based substance, which preferably is betulin or a flavonol, or a mixture thereof for preventing the deposit formation caused by thermophilic adhering bacteria on surfaces of paper or board machines, or to remove such deposits from the said surfaces.

In the following, the invention is described in detail with the aid of laboratory studies and examples. The percentages presented in this specification are percents by weight and those of the solvents are percents by volume.

The studies conducted

Raw extracts of rowan tree, birch, willow, maple and spruce were prepared from chopped branches (the order of size 0.5 – 2 cm). Bark of a conifer was ground so as to obtain a similar size before extraction. The parts of both lingonberry and blueberry above ground were taken to the extraction. The extractions were carried out with a mixture of ethanol of about 90% and acetone (about 3%) (Etax B 7 solvent) for about 2 weeks at room temperature. The extracts were concentrated to a dry content of 11 to 30%. The plant extract contents mentioned in the examples refer to the content of raw extract as dry matter.

The adhering bacterium *D. geothermalis,* isolated from a paper machine, was kept frozen at a temperature of -70°C. For the deposit inhibition studies, it was rejuvenated in TH nutrient liquor with agitation at 45°C. The composition of the TH liquor was as follows:

Tryptone	5 g/l
Yeast extract	2.5 g/l
Water	1000 ml
pH	6.8 – 7.0

A total of three inoculations (á 40 ml/24 h) of the rejuvenated deinococcus were added into steel biofilm devices having a liquid volume of about 4 litres. Such biofilm devices are described in the patent publication FI 95597. The initial content of deinococcus in the circulation water of the biofilm devices was $1x10^8$-$5x10^8$ pieces/ml. As circulation liquid, 0.1-percent sterilized paper machine white water was used (thin nutrient liquor in testing the pentahydroxy flavone). It was circulated in the steel (AISI 316) biofilm devices past the sample plates (7.5 x 1.5 cm) by

means of pumps at a speed of about 60 cm/s. The temperature was about 45°C. The value of acidity was kept in a pH area of 6 – 7.5. 8 similar biofilm devices were used, one of which being a control device (deinococcus only) and the other 7 devices were used to test the efficiency of the plant extracts and the plant-based substances (deinococcus + the substance to be tested). A total of 3 dosages of the substances to be tested were added (30 to 500 ppm/24 h as dry matter). The testing time was 3 days. The content of deinococcus was determined from the steel plates by means of a cultivation method. The loose deposits of the steel plates that were taken from the biofilm devices were first washed off for 2 to 3 seconds with sterile spray water (3 bar). After this, the actual deposits were detached into sterile water by means of sterile toothbrushes. The deinococcus was determined from the suspensions thus obtained by cultivation by means of a biological membrane method (0.2 μm, Sartorius) with PCA agar, incubating for 3 days at 45°C. The composition of the PCA agar was as follows:

Tryptone	5 g/l
Yeast extract	2.5 g/l
Glucose	1 g/l
Agar	15 g/l
Water	1000 ml
pH	7.0

The deinococcus content of the steel plate of the control device was 10^5-10^7 pieces/cm^2. The effect of the plant extract and the plant-based substances was obtained by comparing the deinococcus content of the control steel plate (pieces/cm^2) to that of the steel plate of the biofilm device containing the plant extract or the plant-based substance (pieces/cm^2). This difference is indicated as percents in the following examples.

Examples

Example 1

The effect of the plant extract (13% of dry matter) prepared from rowan on the inhibition of deinococcus adhesion was studied in a laboratory by means of steel biofilm devices in accordance with the method described above. The results were as follows:

Plant extract and dosage	Content of deinococcus on steel plate, pieces/cm^2	Inhibition of deinococcus adhesion %
Control	$1.4x10^6$	-
Rowan extract 100 ppm	$1.9x10^5$	86
Rowan extract 250 ppm	$4.4x10^3$	99.7

As the results show, the rowan extract in a content of 100 to 250 ppm was fairly effective in inhibiting the adhesion of deinococcus to steel; particularly, if taking into account the high content of the deinococci, which was to be inhibited, in the circulation water of the biofilm devices ($1x10^8$-$5x10^8$ pieces/ml) and the non-frequent dosing of the substances to be tested (1 dosage/day).

Example 2

The effect of the other plant extracts was studied in quite a similar way than that of the rowan extract in the previous Example 1. The results were as follows:

Plant extract	**Dry content of plant extract %**	**Addition of plant extract ppm**	**Inhibition of deinococcus adhesion %**
Birch[1]	30	50	97.3
"		100	96.7
"		150	99.1
Spruce branches[2]	22	100	98.7
Lingonberry	26	250	94.8
Maple	13	100	92
„		250	97.2
Pine bark	25	50	97.6
Willow	11	100	91.1
"		250	98.2
"		500	98.1
Blueberry	14	500	95

[1] from dried birch branches

[2] from spruce branches decayed for about 10 years

The results indicate that all the plant extracts in Example 2 inhibited the adhesion of deinococcus to steel, when in sufficient concentrations. The most effective ones were the extracts prepared from birch and the bark of pine, which inhibited the

adhesion of deinococcus by about 97% in a content of 50 ppm (as dry matter). The amount of the blueberry extract needed for obtaining a corresponding result was 500 ppm.

Example 3

The ability of the plant-based substances (betulin, pentahydroxy flavone and trihydroxy flavone) to inhibit the adhesion of deinococcus to paper machine steel was studied in the same way as the ability of the plant extracts in Examples 1-2. The results were as follows:

Plant-based substance	**Addition ppm**	**Inhibition of deinococcus adhesion %**
Betulin[1]	50	93
Pentahydroxy flavone	30	99.95
Trihydroxy flavone	100	84

[1] dissolved in acetic acid

Of the plant-based substances studied, the pentahydroxy flavone was thus particularly effective in inhibiting the adhesion of deinococcus to steel.

Reference example 1

For the sake of comparison, the ability of the anti-microbial agent Fennosan M9 (methylene bisthiocyanate as the active ingredient) to inhibit the adhesion of deinococcus to steel surfaces was studied. The study was conducted in a similar way as in the above Examples 1 and 2. The results were as follows:

Fennosan M9 ppm	**Inhibition of deinococcus adhesion %**
20	70
60	99
100	99

According to these results, the amount of the Fennosan M9 product needed was 60 to 100 ppm for effectively preventing the adhesion of deinococcus to steel surfaces. On the basis of the results, it can be concluded that, by means of the best plant extracts, at least as good an inhibition of deinococcus adhesion to steel can be achieved as with that of the anti-microbial agent commonly used in paper machines, namely the methylene bisthiocyanate.

Reference example 2

The effect of eucalyptus oil on the adhesion of the deinococcus bacterium to steel surfaces presented in the patent publication US 6 267 897 B was also studied. The study was conducted in the same way as in the above Examples 1 and 2. The results were as follows:

Content of eucalyptus oil ppm	**Inhibition of deinococcus adhesion %**
100	0
250	37

On the basis of these results, we can conclude that the eucalyptus oil in 100 ppm or 250 ppm had practically no inhibitive effect. In practice, namely an effect of less than about 90% cannot be considered significant. This leads to the conclusion that eucalyptus oil has no effect on the actual adhering bacteria of hot paper machines.

By using, in the paper industry, the plant extracts and the plant-based substances according to the invention, it is possible to accomplish distinct advantages over the present anti-microbial agents: in utilization contents, they may be non-toxic or less toxic for the paper machine bacteria than biocides containing synthetic active ingredients. It is probable that in nature, any plant compounds that are bio-chemically produced degrade more easily and perhaps quicker into organic compounds than compounds, which are made by means of a chemical synthesis and which generally are foreign to the nature. The raw materials of the plant extracts are easy to obtain during the growth period. In a way, the plant extracts are substances of the paper machine's "own", as some of them can actually be prepared from the same wood as paper and board, even though from different parts of the wood and by different methods.

Claims:

1. A method of inhibiting the deposit formation caused by thermophilic adhering bacteria on surfaces of paper or board machines, or removing such deposits from the said surfaces, **characterized** in that a concentration of at least one plant extract or at least one plant-based substance or a mixture thereof is added to the circulation waters of paper or board machines, the concentration being effective against thermophilic adhering bacteria.

2. A method according to Claim 1, **characterized** in that the plant extract originates from any of the following plants or parts of plants: deciduous tree, bark of a conifer, decayed conifer or a woody, shrubby plant.

3. A method according to Claim 1 or 2, **characterized** in that the plant extract originates from any of the following plants or parts of plants: rowan tree, birch, maple, willow, lingonberry, blueberry, bark of pine or decayed spruce branches.

4. A method according to any of the preceding claims, **characterized** in that the said plant extract is obtained by extracting the plant or a part of the plant with ethanol or acetone or a mixture thereof.

5. A method according to Claim 1, **characterized** in that the plant-based substance is a natural substance isolated from a plant, or a synthetic equivalent or derivative thereof.

6. A method according to Claim 5, **characterized** in that the plant-based substance is betulin or a flavonol, such as pentahydroxy flavone or trihydroxy flavone.

7. A method according to any of the preceding claims, **characterized** in that the plant extract or the plant-based substance or a mixture thereof is added to the circulation waters of paper or board machines so as to obtain a product concentration of 1 to 1000 ppm, preferably 10 to 500 ppm, as calculated from the dry weight of the plant extract or the plant-based substance.

8. A method according to any of the preceding claims, **characterized** in that the plant extract or the plant-based substance or a mixture thereof is added to the circulation waters of paper or board machines either 2 to 8 times a day in cycles or in one single dose per day.

9. A method according to any of the preceding claims, **characterized** in that the plant extract or the plant-based substance or a mixture thereof is dosed in single

doses of 500 to 5000 ppm, as calculated from the dry weight of the plant extract or the plant-based substance, into a container for removing adhering bacteria from its surfaces by means of a so-called shock dosage.

10. A method according to any of the preceding claims, **characterized** in that the thermophilic adhering bacterium is *Deinococcus geothermalis*.

11. The **use** of a plant extract or a plant-based substance or a mixture thereof for inhibiting the deposit formation caused by thermophilic bacteria on surfaces of paper or board machines or for removing such deposits from the said surfaces.

12. The use according to Claim 11, **characterized** in that the said plant extract or the said plant-based substance or a mixture thereof is added to the circulation waters of paper or board machines so as to obtain a product concentration of 1 to 1000 ppm, preferably 10 to 500 ppm, as calculated from the dry weight of the plant extract or the plant-based substance.

Abstract

The invention relates a method of inhibiting the deposit formation caused by thermophilic adhering bacteria, *Deinococcus geothermalis* in particular, on surfaces of paper or board machines, or removing such deposits from the said surfaces so that a concentration of at least one plant extract prepared from wood, bushes or woody, shrubby plants, or at least one plant-based substance, such as betulin or a flavonol or a mixture thereof, is added to the circulation waters of paper or board machines, the concentration being effective against thermophilic adhering bacteria.